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16. Abstract

Molecules in certain excited states can be forced to predissociate in an external electric field. This effect will be shown to occur with H_2 and D_2. The molecular dissociation is made possible by an altered coupling mechanism as compared to the mechanism considered for the Kronig's selection rules. The interaction is a linear function of the field strength It is further demonstrated that also molecular fields (van der Waal's fields) may cause the effect which is shown by the collision induced predissociation of the excited molecular states under consideration.

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PREDISSOCIATION IN AN ELECTRIC FIELD—A NEW PHENOMENON IN MOLECULAR SPECTROSCOPY

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It has been known for a long time that molecules can dissoci- /406[*]
ate from bound states (predissociation). These molecular states
are, of course, considered bound only in an approximation which
does not contain all the interactions. But if we include config-
uration into action in the description, which is important for
molecular disintegration, it would be more correct to speak of
quasi-bound states. These quasi-bound states express themselves
in a longer lifetime than the molecular vibration time. This time
can be considered as the maximum lifetime of the molecule with re-
spect to dissociation. But, on the other hand, their lifetime is
shorter than that of spontaneous radiation from deep-lying bound
states. This manifests itself in the spectrum through broadened
lines in the absorption of the quasi-bound states. Their half-
width gives a certain measure for their shortened liftime with re-
spect to the emission of radiation. Their exact description, how-
ever, requires the picture of discrete and continuous states, since
the wave function contains both parts. Not all states which lie
energetically higher than the dissociation limit of the molecule
can dissociate through nonradiative decay. The transition must
meet certain selection rules, known as Kronig's rules. For this
reason it is possible that, for instance, certain rotational states
in a given vibrational band of an electronic excited state can

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decay, but others can not. The latter consequently appear in emission. Similar results are valid for autoionization, which is likewise a form of radiationless decay.

Besides this normal predissociation, there are other forms of predissociation, which can be called induced predissociation. Radiationless decay of a molecule into molecular fragments can be induced by a strong magnetic field. Turner [1] in 1930 found that excited iodine molecules, whose decay is forbidden according to selection rules, can dissociate in a strong magnetic field. Van Vleck [2] gave a theoretical explanation for the problem. A dissociation into two non-excited iodine atoms is possible when the selection rule $\Delta J = 0$ loses its force in a magnetic field. Another phenomenon is called collision-induced predissociation. Turner [3] could observe in his experiments that excited iodine molecules decayed even without a magnetic field when the iodine pressure itself, or the partial pressure of additional gases, was large enough to make an adequate number of collisions probable within the radiative lifetime. The interpretation of this effect has to date not been fully satisfactory. An attempt has been made to base the collision predissociation on the magnetic interaction of the colliding particles [4]. The van der Waals forces have also recently been discussed as a cause [5].

To the already mentioned processes of field induced predissociation a further effect must most recently be added, which is induced by electric fields. We could show that, for instance, excited H_2 molecules can be dissociated by fields of a few volts per cm [6]. In the meantime, the effect has also been demonstrated for D_2, as will be shown in the following.

Experimental Procedure

The proof for the dissociation of hydrogen molecules was already given in our previous research [7], through measurement

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of atomic fluorescence. Dissociation of the molecule generates, among other things, an excited atom whose fluorescence radiation is the Ly_α-emission. The UV-sensitive detector is therefore preceded by an Ly_α filter. The remaining parts of the apparatus are the vacuum UV monochromator, a light source, and the observation chamber. Individual parts of the arrangement have already been explained, so that we can dispense with the description. An important aid for the investigation is a homogeneous electric field which extends over the entire observation chamber. The distance between the field plates could be reduced to 0.5 cm, so that the applied voltage is never higher than 100 volts. The condenser plates themselves consist of very transparent screens (90% transparency). Thus the production of photoelectrons through atomic radiation is avoided. The measuring signal is led in the usual fashion to a counting device with a recorder or a rate meter.

Foundations of the Measurement Procedure and Results

In the following section the procedure will be given for the determination of field predissociation, as well as results for hydrogen molecules. A number of experimental paths are possible for the observation of predissociation in general.

A large number of spectroscopic measurements are based on absorption. Absorption measurements can in principle be used for the observation of predissociation effects. Such a measurement usually produces the initial evidence. The radiationless molecular decay expresses itself, when the resolution is insufficient, in an altered pressure dependence of the absorption coefficient. When the resolving power is adequate, the measurements of the line broadening is a particularly fruitful procedure. In most cases, however, other procedures are more suitable, such as the observation of molecular fluorescence, and its termination in the spectrum [8]. The determination of dissociation products itself
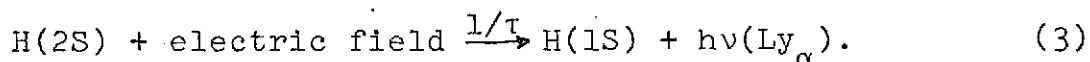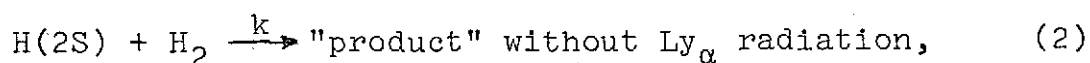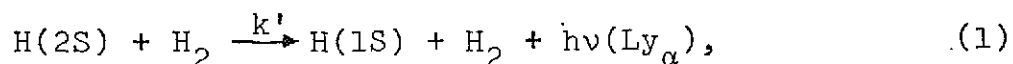
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is naturally a particularly sensitive method, and is particularly suitable when one of the molecular fragments is fluorescent, i.e., in an excited state.

Predissociation of the hydrogen molecules leads to excited H-atoms which give information about their origin through their atomic fluorescence (Ly_α). Since a field-induced effect is present in connection with the measured results to be discussed, the observations are made while applying a suitable electric field. The field effect comes about in this fashion, that excited hydrogen molecules dissociate upon application of a field, although they would not, or nearly not, dissociate in the field-free case. The dissociation in these circumstances is complete, since absorption and dissociation cross-sections nearly coincide in the field. Without a field they are measurably different. The proof of dissociation follows from measurement of the resulting Ly_α-emission. For the proof of field-induced molecular dissociation, it must also be noted that molecular states exist which decay through normal predissociation, even without the application of a field. In this case there generally occur metastable H(2S) atoms. Besides the molecules, these particles too show a field effect. Other processes than field predissociation and the Stark effect mixing of H(2S) and H(2P) do not occur. The latter can lead to a field dependent emission of Ly_α radiation. For the measurement of field induced predissociation, therefore, a method must be used which makes possible separate observation of both field effects. A suitable method results from the different pressure dependence of both effects.

Metastable hydrogen atoms have a long lifetime ($\tau = 1/7$ s) and at the pressures under consideration ($p_{H_2} = 1 \cdot 10^{-2}$ torr) are completely deactivated by collision. Molecular states subject to /408 predissociation in electric fields do not have a long lifetime

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(their lifetime is unknown, but probably lies at about 10^{-6} s).
At the prevailing H_2 pressure they are only minimally affected by
gas kinetic collisions. A better understanding of collision pro-
cesses of metastable hydrogen atoms was obtained in our investi-
gations. For this purpose, preliminary measurements [7] determined
the interaction cross-sections for the deactivation of H(2S) and
D(2S) atoms and their energy dependence in collisions with H_2 or
D_2. Two different processes could be observed here: 1) the col-
lision induced emission of Ly_α and 2) the "reactive" collision,
which led to the extinction of atomic fluorescence.

The simplified reaction scheme is as follows

$$H(2S) + H_2 \xrightarrow{k'} H(1S) + H_2 + h\nu(Ly_\alpha), \tag{1}$$

$$H(2S) + H_2 \xrightarrow{k} \text{"product" without } Ly_\alpha \text{ radiation,} \tag{2}$$

$$H(2S) + \text{electric field} \xrightarrow{1/\tau} H(1S) + h\nu(Ly_\alpha). \tag{3}$$

For fields which are not too large the following is valid [9]

$$1/\tau = AF^2 \tag{4}$$

where F is the electric field strength.

The measurable Ly_α intensity, according to this scheme, is

$$K(Ly_\alpha) \sim \frac{k'[H_2] + AF^2}{(k'+k)[H_2] + AF^2}. \tag{5}$$

From equation (5) the rate constants and consequently the inter-
action cross-sections of equations (1) and (2) can be calculated.
The cross-section for equation (1) is energy-dependent. Accord-
ingly, for kinetic energies of the excited hydrogen atoms, such
as result through photo-dissociation in the wavelength region
between 810 and 820 Å, between 1/5 and 1/6 of the primary gener-
ated metastable atoms are quenched through reactive collisions (2).

If the observation chamber is put into an electric field, then the metastable atoms have a field-dependent lifetime (3), which, with increasing field, influences the competition between collision deactivation and spontaneous emission in such a way as to favor the latter. If the field is large enough, the metastables radiate their energy in the form of Ly_α. The largest possible increase in the observation region is about 25% for atoms at $p_{H_2} = 1 \cdot 10^{-2}$ torr. If in the electric field increases are measured which are significantly larger than 25%, then only a field-induced molecular decay can be responsible, according to the preceding considerations. Measurements on H_2, however, gave observed increases of up to 350% [6].

As we have already explained in a previous paper [6], field decay is produced by configuration mixing in the electric field. This opens new decay paths for dissociation. The matrix elements are only non-zero when the states have unequal parity in the field-free case. Since the mixing states always experience some change in character, the application of first-order perturbation theory gives an interaction which depends linearly on the field strength. The test of the linear dependence of the interaction on the field strength is therefore an important characteristic for the explanation of field predissociation.

Figure 1 shows the measured $Ly_\alpha(D)$ fluorescence of excited D atoms, from dissociation of D_2 with or without an electric field. Especially important is the spectrum shortly before the D-X(7.0) band. As in the case of H_2, an increase is present here which far exceeds the measure of the field effect to be expected from metastable D atoms. The effect is particularly clear in the position $\lambda = 808.9$ Å. The increase in Ly_α radiation in the field is here 80%.
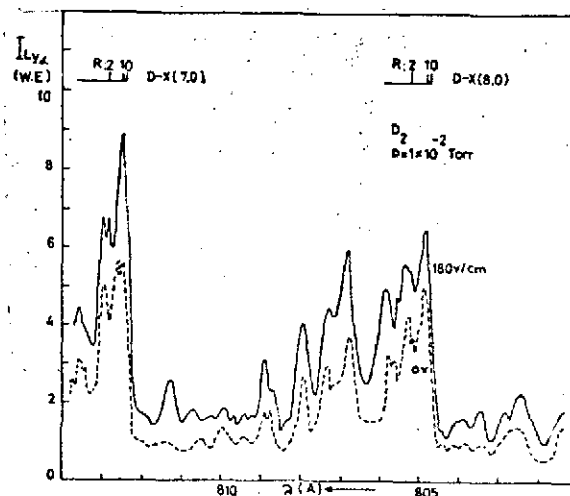
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Fig. 1.   Intensity of Ly_α-(D) fluorescence as a function
of wavelength of the exciting primary radiation,
with and without electric field. D_2 pressure:
$1 \cdot 10^{-2}$ torr.   Band with of the primary radiation
0.25 Å.

For this excitation state the field dependence of the effect
was also measured (Fig. 2).   It is clearly different from the
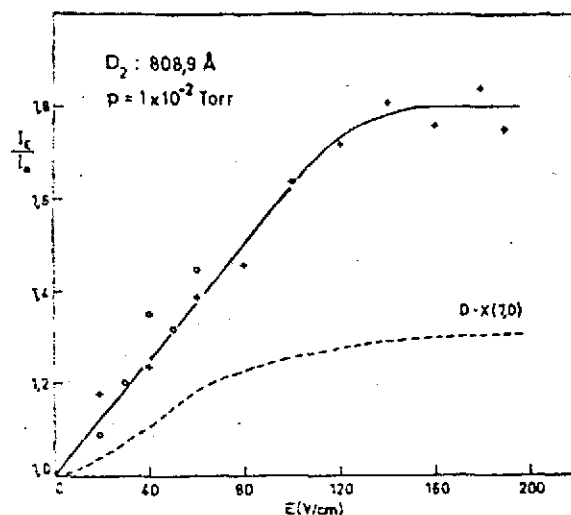behavior of meta-stable D atoms in the field (lower curve).

Fig. 2.   Field strength dependence of the Ly_α-(D) fluores-
cence, measured for the position $\lambda_{primary}$ = 808.9 Å
at a D_2 pressure of $1 \cdot 10^{-2}$ torr.

An interesting indication of the nature of the field dissociating molecular states can be gathered primarily from the H_2 spectrum. The spectrum can more easily be resolved than the D_2 spectrum because of its greater level separations. H_2 measurements are therefore shown in Fig. 3. These refer to the region of the ionization continuum, where a particularly strong field effect was observed.
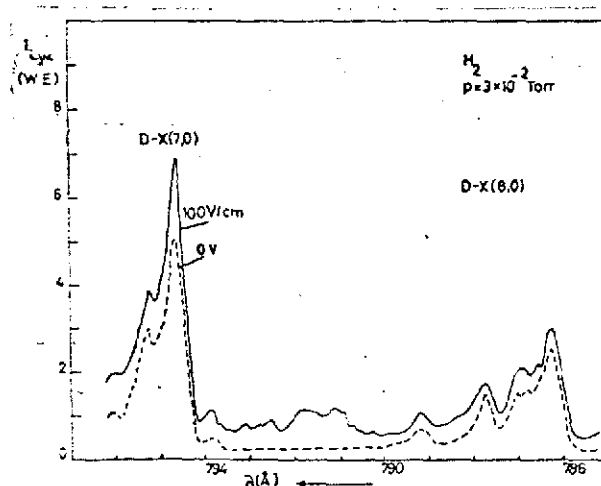

Fig. 3. Intensity of the Ly_α(H) fluorescence as a function of wavelength of the exciting primary radiation in the region of the ionization continuum of H_2.
Technical data as in the measurements of Fig. 1.

A noticeable portion of the absorption a little above the ionization limit can still be ascribed to dissociative processes. This portion is structureless, particularly between 790 and 793.5 Å. As soon as a field is applied, the Ly_α radiation increases strongly and reaches an increase of 350% for 150 volts/cm. A similar absorption, which produces dissociation of the molecule, is also measured between 804 and 799 A. Here too the dissociation cross-section is without recognizable structure. But it remains structureless even upon application of the field. The measurement

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shows, among other things, that the charge carriers which are formed by photoionization in this region, have no influence on the measurements in the electric field. Even though the ionization cross-section is strongly structured, fluorescence measurements are not affected by this.

The measurement of D_3^+ formation to chemi-ionization of excited D_9 molecules is extremely instructive. The D_2 spectrum which is mirrored in the ionization curve remains simple despite the high excitation energies, so that participation of high Rydberg states must be suspected, as is the case with H_2. A discussion of these results, however, will be postponed until a highly resolved D_2 spectrum is available in this energy region.

Discussion

The measured results of Fig. 1 clearly show that the field predissociation effect, already found for H_2, also appears with the D_2 molecule. The increase of the measured Ly_α radiation in the electric field is much greater (up to 180%) than can occur in this wavelength region for fluorescing photodisocciation products such as D(2S) (25%). Since H_2 and D_2 have the same electron structure, we also expect that similar processes are possible in principle. But because of their large mass, the dissociation process, which competes with molecular fluorescence, will occur more slowly. It therefore would not be surprising to measure a smaller effect with D_2 than with H_2. But we cannot give an unambiguous explanation along these lines, since the D_2 spectrum is much more poorly resolved than the H_2 spectrum. Within bandwidths of the incident primary light, significantly more excited states of the molecules are formed.

According to the measured results for light hydrogen [6],   /410 first consideration for the field decay belongs to the vibrationless states of the Rydberg series with $^1\Sigma_u^+$-configuration. The

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position of these states is well-known through very recent absorption measurements. For deuterium measurements, the determination of this kind of state is much more difficult in principle, because of the strong level overlap. A measurement of the D_2 absorption cross-section ($\Delta\lambda = 0.08$ Å) is indeed available in this wavelength region [10], but the resolution is inadequate to analyze the D_2 spectrum. Measurements at substantially higher resolving power [11] have not yet been evaluated, so that at this time they can not be applied for the analysis of the levels that are of importance here.

While the electronic states of the isotopic molecules H_2 and D_2 differ only slightly from one another, the difference for vibrational and rotational spectra is much greater. The mass enters the vibrational energy according to its root, and it enters the rotational energy linearly. This leads to smaller band separation and most of all to a fuller thermal occupation of the rotational space. At room temperature, 66.1% of the H_2 molecules are in the rotational state $J'' = 1$, while the states with $J'' = 0$ and $J'' = 2$ are occupied only 13.1% and 11.6%, respectively. For D_2 this balance is shifted to 18.4%, 20.6%, and 38.5%, for the states $J'' = 0$, 1, and 2 (T = 300° K).

The deuterium spectrum is therefore much denser in absorption lines. This also expresses itself in the measurement of field predissociation. Since field decay depends on the excited state of the molecule, only increases can generally be observed which are mediated through several states.

The measured increase in predissociation in the electric field—shown here for $\lambda_{primary}$ = 808.9 Å—is, according to Fig. 2, is first a linear function of the applied field strength. In this the effect is clearly different from the behavior of metastable D(2S) atoms in a field. For both particles, the lifetime with

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respect to predissociation or Ly_α emission decreases quadratically with field strength. Deactivation of the states of both particles is described by quite similar equations (see [4]). The excited molecules have a short lifetime. Without a field they will consequently in most cases make transitions through molecular fluorescence to deeper lying states or to the ground state. The weak competition through deactivation in gas kinetic collisions permits an increase in the field which is practically linear with field strength. The existence of a pseudo-linearity here can be demonstrated at higher pressures. For the long-lived metastable atoms by contrast, the competition through collisions is fully effective, resulting in an apparently different field dependence. The effect of metastable atoms and the effect of excited molecules in an electric field can easily be distinguished through this pressure-dependent effect. In a field strength of 150 volts/cm the saturation value is already reached for the field increase of the molecules.

The measured result showed in Fig. 3 is interesting. The radiated Ly_α emission in the region between 793.5 and 790 Å is structureless without a field. This raises the suspicion that the excited H atoms arise by a direct transition of the molecular system into the dissociation continuum. The dissociation cross-section without the field at $3 \cdot 10^{-2}$ torr is about 4% of that for the D-X(7.0) band. Since atomic fluorescence in the field (180 volts/cm) nearly agree with the total absorption, up to the ionization cross-section, this curve yields a comparison with highly resolved absorption measurements. According to Takezawa [12], the following states must be considered in this region.

1. Rydberg terms of the series $^1\Pi_u$ and $^1\Sigma_u^+$ (v' = 1) with $n \geq 13$. The convergence limit of both series lies at 790 Å. The higher members below 791 Å have not been observed in absorption.

2. Between 791 Å and 792 Å occur the states n = 7 of $^1\Sigma_u^+$ (v' = 2) as well as n = 5 $^1\Pi_u$ (v' = 3). A strong increase of Ly_α intensity in the field is observed here. It must therefore be assumed that particularly the $^1\Sigma_u^+$ state participates in the field decay. This would establish a connection which qualitatively agrees with the assertions of previous research. Herein the $^1\Sigma_u^+$ state with n ≥ 9, of the vibrationless ground state of the H_2^+ converging Rydberg series, was made responsible for the field effect /411 [6].

Let us compare the measurements between 794 Å and the ionization limit (804 Å) with this finding. In the region from 799 to 804 Å a structureless dissociation cross-section has also been measured here. This corresponds to about 3-4% of the cross-section measured for D-X(6.0). In this region Rydberg states occur with n ≤ 9 [12]. But the increase in a field is structureless, and so we draw the conclusion that these states predissociate in the field either not at all or only a little. This result agrees well with measurements of field of decay of the vibrationless $^1\Sigma_u^+$ state before the ionization limit. The field effect begins with larger princple quantum numbers, beginning with n = 10.

Our own [10] as well as other authors' [13] measurements show that the coupling in H_2 goes over from Hund's case b to case d, as the principle quantum number increases. The measured separations of the levels K = 0 and K = 1 of the Σ-states first increased and then decreased strongly [12]. The position of both levels are almost identical for n = 9, and then exchange their sequence. The field-induced decay of the molecule likewise begins with these states. Among other things, the electric field destroys the symmetry of the system. Now states of g-symmetry can couple with the Σ_u-states [2], which opens new paths for predissociation. The matrix elements are linear in the field strength. For this new

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path of dissociation it must, however, be presupposed that the potential curve of the final state has a suitable position with respect to the Σ-state that may then be excited. The conception that macroscopic electric field can cause predissociation in molecules is also supported by measurements of collision-induced predissociation [14]. We have recently succeeded through induced predissociation, by collisions with suitable atoms and molecules, of the H_2 states which underlie field decay.

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